(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 431 409 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
05.07.2006 Bulletin 2006/27

(51) Int Cl.:
C22C 38/60 (2006.01) *C22C 38/40 (2006.01)*
C22C 38/28 (2006.01) *C22C 38/18 (2006.01)*
C22C 19/05 (2006.01) *C22C 27/06 (2006.01)*

(21) Application number: **04004043.8**

(22) Date of filing: **01.09.2000**

(54) **Free cutting alloy**

Automatenlegierung

Alliage de décolletage

(84) Designated Contracting States:
DE FR GB SE

(30) Priority:
03.09.1999 JP 25090299
14.03.2000 JP 2000070257
21.07.2000 JP 2000221433
22.08.2000 JP 2000251602
22.08.2000 JP 2000251626

(43) Date of publication of application:
23.06.2004 Bulletin 2004/26

(62) Document number(s) of the earlier application(s) in accordance with Art. 76 EPC:
00118990.1 / 1 085 105

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(56) References cited:
- **PATENT ABSTRACTS OF JAPAN vol. 009, no. 324 (C-320), 19 December 1985 (1985-12-19) -& JP 60 155653 A (HITACHI SEISAKUSHO KK), 15 August 1985 (1985-08-15)**

Description

[0001] Alloy has widespread applications because of a variety of characteristics thereof. A free cutting alloy excellent in machinability is, in a case, selected for improvement of productivity. In order to improve machinability, for example, free cutting alloy containing an element improving machinability such as S, Pb, Se or Bi (hereinafter referred to as machinability-improving element) is widely used. Especially in a case where machinability is particularly required because of precise finishing in machining or for other reasons, not only is a content of such a machinability-improving element increased in an alloy, but the elements are also added to an alloy in combination.

[0002] While S, which has widely been used for improvement of machinability, is in many cases added in the form of MnS, addition thereof in an alloy in a large content causes for degrading corrosion resistivity, hot workability and cold workability of the alloy. Moreover, when the alloy is exposed to the air, a sulfur component included in the alloy is released into the air in the form of a sulfur containing gas, which causes sulfur contamination in peripheral areas of parts with ease. Therefore, there arises a necessity of suppressing release of sulfur containing gas (hereinafter referred to as improvement on out-gas resistivity). Elements such as S, Se and Te, however, deteriorate magnetic properties to a great extent in an electromagnetic stainless steel and the like.

[0003] Therefore, various proposals have been made: a Mn content is limited, a Cr content in sulfide is increased or in a case where S is contained, Ti is added in combination with S in order to disperse sulfide in the shape of a sphere (for example, see JP-A-98-46292 or JP-A-81-16653). To increase a Cr content in sulfide, however, tends to greatly decrease in machinability and hot workability and therefore, such a alloy has been restricted on its application in many cases.

[0004] JP 60155653 enables the production of an iron-base super alloy having excellent high temperature strength, toughness and high temperature ductility by melting an Ni-Cr alloy steel in a vacuum atmosphere, decreasing considerably the content of oxygen and hydrogen and adding a specific desulfurizing agent to decrease the content of S.

[0005] It is accordingly an object of the present invention is to provide free cutting alloy excellent in machinability, showing outstanding characteristics as an alloy such as corrosion resistivity, hot workability and cold workability or specific magnetic characteristics, which are comparable to those of conventional alloys.

[0006] In order to achieve the above described object, a free cutting alloy of the present invention is characterized by the free cutting alloy of claim 1. " (Ti,Zr)" means one or two of Ti and Zr.

[0007] Machinability of an alloy can be improved by forming the above described (Ti, Zr) based compound in a matrix metal phase of the alloy. Furthermore, by forming this compound in the alloy, formation of compounds such as MnS and CMn,Cr)S, easy to reduce corrosion resistivity and hot workability of the alloy, can be prevented or suppressed, thereby enabling corrosion resistivity, hot workability and cold workability to be retained at good levels. That is, according to the present invention, a free cutting alloy excellent in machinability can be realized without any degradation in useful characteristics as an alloy such as hardness, corrosion resistivity, hot workability, cold workability and specific magnetic characteristics.

[0008] Further, a (Ti,Zr) based compound formed in a free cutting alloy of the present invention is dispersed in the alloy structure. Machinability of an alloy can be further increased especially by dispersing the compound in an alloy structure. In order to increase the effect, a particle size of the (Ti,Zr) based compound as observed in the structure of a polished section of the alloy is preferably, for example, approximately in the range of 0.1 to 30 μm on the average and further, an area ratio of the compound in the structure is preferably in the range of 1 to 20 %, wherein the particle size is defined by the maximum distance between two parallel lines circumscribing a particle in observation when parallel lines are drawn intersecting on a region including the particle in observation while changing a direction of the parallel lines.

[0009] The above described (Ti,Zr) based alloy can include at least a compound expressed in a composition formula $(Ti,Zr)_4(S,Se,Te)_2C_2$ (hereinafter also referred to as carbo-sulfide/selenide), wherein one or more of Ti and Zr may be included in the compound and one or more of S, Se and Te may be included in the compound. By forming a compound in the form of the above described composition formula, not only can machinability of an alloy be improved, but corrosion resistivity is also improved.

[0010] It should be appreciated that identification of a (Ti,Zr) based compound in an alloy can be performed by X-ray diffraction (for example, a diffractometer method), an electron probe microanalysis method (EPMA) and the like technique. For example, the presence or absence of the compound of $(Ti,Zr)_4(S,Se,Te)_2C_2$ can be confirmed according to whether or not a peak corresponding to the compound appear in a diffraction chart measured by an X-ray diffractometer. Further, a region in the alloy structure in which the compound is formed can also be specified by comparison between two-dimensional mapping results on characteristic X-ray intensities of Ti, Zr, S, Se or C obtained from a surface analysis by EPMA conducted on a section structure of the alloy.

Brief Description of the Drawings

[0011]

Fig. 1 is a graph showing an X-ray diffraction chart of reference steel specimen No. 5 in experiment of Example 1 (Reference);

Fig. 2 is a graph showing an example of Schaeffler diagram;

Fig. 3 is an optical microphotograph of the reference steel specimen No.5 in Example 1 (Reference);

Fig. 4 is a graph showing dependencies of solubility products on temperature of components of TiO, TiN, $Ti_4C_2S_2$, TiC, TiS and CrS in γ-Fe;

Fig. 5 is an optical microphotograph of a fifth selection inventive steel specimen No. 30 in Example 2,

Fig. 6 is a graph showing a relation between a range of parameters of X and Y and evaluation results on hot workability in Example 2; and

Fig. 7 is a graph showing a relation between a drill boring time and Y in mass % of an alloy in Example 2.

Preferred Embodiments of the Invention

[0012] The present invention, to be concrete, can be preferably applied on an alloy constituted as stainless steel. In this case, in order to form a (Ti,Zr) based compound without any degradation in characteristics as stainless steel, such an alloy preferably contains one or more of Ti and Zr such that W_{Ti} + 0.52 W_{Zr} fulfills the formula in claim 1, wherein W_{Ti} and W_{Zr} denote respective contents in mass % of Ti and Zr; and one or more of S, Se and Te. Reference is made to claim 1.

[0013] Ti and Zr are indispensable elements for forming a (Ti,Zr) based compound playing a central role in exerting the effect of improving machinability of a free cutting alloy of the present invention. The above effect exerted when Ti and Zr are added into an alloy is determined by the sum of the numbers of atoms (or the sum of the numbers of values in mol), regardless of kinds of metals, Ti or Zr. Since a ratio between atomic weights is almost 1 : 0.52, Ti of a smaller atomic weight exerts a larger effect with a smaller mass. Thus, a value of W_{Ti} + 0.52 Wzr is said to be compositional parameter reflects the sum of the numbers of atoms of Zr and Ti included in an alloy.

[0014] Further, the present invention can be preferably applied for (Fe, Ni) based electromagnetic alloy, (Fe, Ni) based heat resisting alloy and (Fe,Ni) based alloy such as Invar alloy, Elinvar alloy and the like with a small thermal expansion coefficient, a small thermal coefficient of an elastic modulus in room temperature, for use in precision machine parts (hereinafter referred to as a fifth selection invention). In Ni based electromagnetic alloy, the alloy including 20 to 80 mass % Ni is generally used, and there can be exemplified as the alloy; for example, alloys called Permalloy or Perminver. Ni heat resisting alloy including 40 to 80 mass % Ni is widely used.

[0015] The fifth selection invention of the present invention constituted as (Fe, Ni) based electromagnetic alloy, (Fe, Ni) based heat resisting alloy or the like can contain 20 to 82 mass % Ni; and the balance mainly consists of one or more of Fe and Cr; further containing: one or more of Ti and Zr in the range satisfying a relation of $0.05 \leq X \leq 3$ (hereinafter referred to as a condition formula (1)),

one or more of S, Se and Te in the range satisfying a relation of 0.01 ≤ Y s 0.5 X (hereinafter referred to as a condition formula (2)),

C in the range satisfying a relation of $0.2 Y \leq Wc \leq 0.3$ (hereinafter referred to as a condition formula (3)), wherein when a Ti content is indicated by W_{Ti} in mass %, a Zr content by Wzr in mass %, a C content by Wc in mass %, a S content by Ws mass %, a Se content by W_{Se} and a Te content by W_{Te}, the following formulae (1) and (2) are given in order to define X and Y:

$$X\ (\text{mass }\%) = W_{Ti} + 0.52\ W_{Zr}$$

(hereinafter referred to as Formula (1)) and

$$Y\ (\text{mass }\%) = W_S + 0.41\ W_{Se} + 0.25\ W_{Te}$$

(hereinafter referred to as Formula (2)) and further one or more of Si, Mn and Al in the respective ranges of 1 mass % for Si; 1 mass % for Mn; and 1 mass % for Al.

[0016] The present inventors had findings that in (Fe, Ni) based alloy for use in electromagnetic material and/or heat resistant material (for example Ni or Fe based heat resistant alloy of a solid solution strengthening type), (Ti,Zr) based compound (for example, a compound in the form of $(Ti,Zr)_4(S,Se,Te)_2C_2)$) is formed and thereby, machinability of the alloy is improved. Further findings were added thereto that while some of indispensable elements constituting the (Ti, Zr) based compound acts a harmful influence, such as degradation in performances of electromagnetic material and/or heat resistant material, on the alloy, such a harmful influence can be deleted if a prescribed condition is imposed on

contents of the indispensable elements of the (Ti,Zr) based compound, thereby enabling machinability to improve while maintaining excellent performances as the electromagnetic material and/or the heat resistant material.
That is, a free cutting alloy of the present invention with the following composition is excellent in machinability and hot workability without deterioration in excellent performances as electromagnetic material and/or heat resistant material, the composition being:

one or more of Ti and Zr in the range satisfying a relation of $0.05 \leq X \leq 3$ (hereinafter referred to as a condition formula (I)),
one or more of S, Se and Te in the range satisfying a relation of 0.01 ≤ Y s 0.5 X (hereinafter referred to as a condition formula (2)),
C in the range satisfying a relation of $0.2\ Y \leq Wc \leq 0.3$ (hereinafter referred to as a condition formula (3)), wherein when a Ti content is indicated by W_{Ti} in mass %, a Zr content by W_{Zr} in mass %, a C content by Wc in mass %, a S content by Ws mass %, a Se content by W_{Se} and a Te content by W_{Te}, the following formulae (1) and (2) are given in order to define X and Y:

$$X\ (\text{mass }\%) = W_{Ti} + 0.52\ W_{Zr}$$

(hereinafter referred to as Formula (1)) and

$$Y\ (\text{mass }\%) = W_{S} + 0.41\ W_{Se} + 0.25\ W_{Te}$$

(hereinafter referred to as Formula (2)).

[0017] Description will be given of the reason why the elements, contents thereof and condition formulae are selected or determined as follows:

(1) 20 to 82 mass % Ni A free cutting alloy of the fifth selection invention of the present invention includes (Fe,Ni) based electromagnetic alloy and (Fe,Ni) based heat resisting alloy. Accordingly, Ni is an indispensable element for the free cutting alloy of the fifth selection invention of the present invention. Further, (Fe,Ni) based electromagnetic alloy and (Fe,Ni) based heat resisting alloy are widely employed with content of the range of 20 to 82 mass % for Ni and since the alloys including Ni in content of this range are particularly required improvement on machinability, the Ni content is limited to the range.

(2) one or more of Ti and Zr in content satisfying a relation of $0.05 \leq X \leq 3$ (hereinafter referred to as a condition formula (1))
When Ti and Zr are added in the above described range together with C, S, Se and Te, (Ti,Zr) based compounds, for example, mainly $(Ti,Zr)_4(S,Se,Te)_2C_2$ and/or a small amount of (Ti,Zr)(S,Se,Te), are formed and therefore, Ti and Zr are useful for improvement on machinability. Moreover, since formation of (Mn,Cr,Ni)S, especially NiS, is suppressed, Ti and Zr are also useful for prevention of cracking in hot working and the free cutting alloy of the fifth selection invention can maintain excellent characteristics as (Fe,Ni) based electromagnetic alloy or (Fe,Ni) based heat resisting alloy such as a thermal expansion coefficient, an elastic constant, magnetic characteristics or a high temperature strength. While Ti and Zr is required to be included in the range of 0.05 mass % or higher in X of a compositional parameter in order to attain an effect of improving machinability, X in excess of 3 mass % is not preferable since when X is in excess of 3 mass %, a specific refining method is required, being accompanied with poor productivity. Accordingly, the range of the parameter X is preferably set in the range of 0.05 to 3 mass % and more preferably in the range of 0.1 to 0.5 mass %. Further, when Ti and Zr are included in the range satisfying the condition formula(I), either one of Ti and Zr or both Ti and Zr may be included.

(3)
One or more of S, Se and Te in contents satisfying a relation of $0.01 \leq Y \leq 0.5\ X$ (hereinafter referred to as a condition formula (2))
S, Se and Te are indispensable elements for formation of the above described (Ti, Zr) based compound. Therefore, the elements are indispensable components for improvement on machinability and are required to be included in the range of 0.01 mass % or higher in terms of the parameter Y. When the elements are added in excess, a compound not useful for improving machinability is formed and in a case, performances of the alloy are deteriorated. Therefore,

when the parameters X and Y are related so as to satisfy the above described condition formula (2), that is when the parameter Y corresponding to a total number of S, Se and Te atoms is half the parameter X corresponding to a total number of Ti and Zr atoms, an additive amount of one or more of S, Se and Te is not excessive but falls within the proper range in amount and therefore, formation of a compound not useful for improvement on machinability can be suppressed and deterioration in performances of the alloy can be prevented or suppressed. As far as S, Se and Te are included in the ranges to satisfy the condition formula (2), either only one of them or two or more of them may be included in the alloy.

(4) C in content satisfying a relation of $0.2\ Y \leq Wc \leq 0.3$ (hereinafter referred to as a condition formula (3))
C forms (Ti,Zr) based compound in co-existence with Ti and Zr, and S, Se and Te and, it is an indispensable, element for improvement on machinability. Moreover, C acts usefully for prevention of cracking occurrence in hot workability. Especially, since C accelerates formation of $(Ti,Zr)_4(S,Se,Te)_2C_2$ more stable than (Ti,Zr)(S,Se,Te), improvement by C on machinability is more effective. It is necessary to include C so as to satisfy the condition formula (3) for achievement of the effects. That is, C is required to be included in the range of at least more than 0.2 times the parameter Y(a parameter on which a total number of S, Se and Te atoms is reflected). When a C content Wc is $Wc < Y/5$, the C content is excessively small, the effect of improving machinability cannot be acquired. On the other hand, an excessive addition of C is not preferable since such a C content causes deterioration in performances of Ni based electromagnetic alloy and Ni based heat resisting alloy. Accordingly, the C content W_C is preferably limited to 0.3 mass % or lower. When the C content exceeds 0.3 mass %, loss of performances of Ni based alloy becomes large. The C content is desirably set in the range of Y/4 to 0.2 mass % and more desirably in the range of Y/4 to Y/2 mass %.
The fifth selection invention of the present invention constituted as (Fe,Ni) based alloy contains one or more of Si, Mn and Al in the respective ranges of 1 mass % or lower for Si; 1 mass % or lower for Mn; and 1 mass % or lower for Al. Description will be given of the reason why the elements and contents thereof are selected as follows:

(5) 1 mass % or lower Si
Si is an element useful as a deoxidizing agent and in addition, for adjustment of hardness and electric resistivity and accordingly, added depending on a necessity. However, when an additive amount of Si is in excess, hardness after heat treatment for solid solution is excessively high, which disadvantageously brings poor workability. Characteristics such as thermal expansion, an elastic constant, magnetic characteristics, heat resistance (high temperature strength) and the like are degraded in some cases. Accordingly, the Si content is limited to 1 mass % as the upper limit and when cold workability is regarded as an important requirement, the Si content is preferably set to 0.5 mass % or lower.

(6) 1 mass % or lower Mn
Mn is an element useful as an deoxidizing agent and further, since Mn forms a compound excellent in machinability in co-existence with S and Se, Mn is added to alloy according to a requirement especially when machinability is regarded as important. The Mn content is desirably set to 0.1 mass % or higher in order to attain more conspicuousness of the effect. On the other hand, when added in excess, corrosion resistivity and cold workability are degraded and deterioration sometimes occurs in characteristics such as thermal expansion, an elastic constant, magnetic characteristics, heat resistivity (high temperature strength) and the like as well. Accordingly, the Mn content is preferably limited to 1 mass % or lower and more desirably to 0.5 mass % or lower.

(7) 1 mass % or lower Al
Al is an element useful as a deoxidizing agent and added to alloy in necessary since Al is effective for adjustment for hardness and electric resistivity. However, when added in excess, deterioration sometimes occurs in characteristics such as thermal expansion, an elastic constant, magnetic characteristics, heat resistivity (high temperature strength) and the like. Accordingly, the A1 content is limited to 1 mass % or lower.
Further, the above described free cutting alloy using (Fe,Ni) based alloy as base can contain Mo or Cu in the ranges of 7 mass % or lower for Mo; and 7 mass % or lower for Cu. Description will be given of the reason why the elements and contents thereof are selected as follows:

(8) 7 mass % or lower Mo
Mo is an element useful for improvement on corrosion resistivity and strength. When the effects are desired to be conspicuous, Mo is preferably included in the range of 0.2 mass % or higher. On the other hand, when added in excess, not only is hot workability deteriorated, but cost-up also occurs and furthermore, deterioration sometimes occurs in characteristics such as thermal expansion, an elastic constant, magnetic characteristics, heat resistivity (high temperature strength) and the like, Accordingly, the Mo content is preferably limited to 1 mass % or lower and

more desirably to 0.7 mass % or lower.

(9) 7 mass % or lower Cu
C is not only useful for improvement on corrosion resistivity, especially in an environment of a reducing acid, but effective for improvement on moldability, decreasing work hardenability. Moreover, since an antibacterial property can also be improved by heat treatment or the like processing, Cu may be added to the alloy according to a necessity. However, since when added in excess, hot workability decreases, the Cu content is preferably set to 7 mass % or lower and especially when hot workability is regarded as important, the Cu content is desirably suppressed to 4 mass % or lower.

[0018] Further, a free cutting alloy of the present invention can contain 12 mass % or lower Cr and moreover, 18 mass % or lower Co. For example, in 30-40 Ni-Fe alloy, magneto-striction acts so as reduce a volume in company with reduction in spontaneous magnetization, which cancels thermal expansion in the ordinary sense. Especially, 36 at % Ni-Fe alloy is generally called Invar alloy and a thermal expansion coefficient in the vicinity of environment temperature is very small, which makes the alloy find a practically important application. The alloy is in many cases used in precision machine material such as of a spring for a measuring instrument. By adding Cr or Co to such an alloy, it is possible to effectively control a thermal expansion coefficient and an elastic constant and thereby, desired performances to match with an intended application can be attained. While Cr is more effective for control of an elastic constant and Co is more effective for control of a thermal expansion coefficient, the elements are not limited to the use in the controls. When Cr or Co are added in excess of the respective above described ranges, an unfavorably large change occurs in compositional conditions on the elements of Ti, Zr, S, Se, Te and C associated with formation of $(Ti,Zr)_4(S,Se,Te)_2C_2$. Accordingly, the Cr and Co contents are set to 12 mass % or lower and 18 mass % or lower, respectively.

[0019] Materials to which the present invention can be applied are in a concrete manner exemplified in trade names among Permalloy generally used as high permeability material, Perminvar used as iso-permeability magnetic material and functional material such as alloy excellent in invar characteristics represented by Invar, and in addition solid·solution strengthening type heat resisting material. It should be appreciated that in the case of stainless steel, an alloy composition means a composition in which part of Fe and Ni as main components is replaced with the elements of Ti, Zr, S, Se, C and the like effective for improvement on machinability in the compositional ranges defined in the present invention. Accordingly, while trade names are employed, alloys under the trade names mean alloys specific to the present invention composed with the alloys of compositions under product specifications as a base only (it should be appreciated that the alloy compositions inherent in products under respective trade names are described in a literature (Revised 3rd Version Kinzoku (Metal) Data Book published by Maruzen, p 223), therefore detailed description thereof is omitted):

(1) High permeability materials including 78-Permalloy, 45-Permalloy, Hipernik, Monimax, Sinimax, Radiometal, 1040 Alloy, Mumetal, Cr-Permalloy, Mo-Permalloy, Supermalloy, Hardperm, 36-Permalloy and Deltamax;
(2) Iso-permeability alloy including 25-45 Perminvar, 7-70 Perminvar, 7-25-45 Perminvar, Isoperm and Senperm;
(3) Invar alloy including Invar, Superinvar, Stainlessinvar, Nobinite alloy and LEX alloy;
(4) Elinvar alloy including Elinvar, EL-1, EL-3, Iso-elastic, Metelinvar, Elinvar Extra, Ni-Span C-902, Y Nic, Vibralloy, Nivarox CT, Durinval I, Co-Elinvar and Elcoloy IV;
(5) Fe based super heat resisting alloy including Haynes 556, Incoloy 802, S-590, 16-25-6 and 20-CB3; and
(6) Ni based heat resisting alloy including Hastelloy-C22, Hastelloy-C276, Hastelloy-G30, Hasteolloy X, Inconel 600 and KSN.

Examples

[0020] The following experiments were performed in order to confirm the effects of the present invention. It should be appreciated that in the following description, test alloy relating to the present invention is referred to as inventive steel or inventive alloy, or as a selection inventive steel or a selection inventive alloy.

Example 1 Ferrite containing stainless steel (Reference only)

[0021] The effects of a free cutting alloy constituted as ferrite containing stainless steel (a reference steel) were confirmed by the following experiment. First, 50 kg steel blocks with respective compositions in mass % shown in Table 1 were molten in a high frequency induction furnace and ingots prepared from the molten blocks were heated at a temperature in the range of from 1050 to 1100°C and the ingots were forged in a hot state into rods with a circular section of 20 mm diameter and the rods were further heated at 800°C for 1 hr, followed by air cooling (annealing) as a source for test pieces.

Table 1

[0022] While main inclusions of a reference steel was $(Ti,Zr)_4(S,Se)_2C_2$, other inclusions such as (Ti,Zr)S and $(Ti,Zr)S_3$ are locally recognized in the matrix. Further, in a specimen No. 7 high in Mn content, (Mn, Cr)S is recognized, though in a trace amount. An identification method for inclusions was performed in the following way: A test piece in a proper amount was sampled from each of the rods. A metal matrix portion of the test piece was dissolved by electrolysis using a methanol solution including tetramethylammonium chloride and acetylaceton at 10 % as a electrolytic solution. The electrolytic solution after the electrolysis was subjected to filtration and compounds not dissolved in steel were extracted from the filtrate. The extract was dried and subjected to chemical analysis by an X-ray diffraction method with a diffractometer. A compound was identified based on peaks of a diffraction chart. A composition of a compound particle in the steel structure was separately analyzed by EPMA and a compound with a composition corresponding to a compound observed by X-ray diffraction was confirmed based on formation from two dimensional mapping results. Fig. 1 shows an X-ray diffraction chart of a reference steel No. 5 by a diffractometer and Fig. 3 is an optical microphotograph of a reference steel specimen No. 5. Further, specimens Nos. 1 to 14 in Table 1 are kinds of steel corresponding to the reference steel and specimens Nos. 15 to 28 are kinds of steel as comparative examples.

[0023] The following experiments were performed on the above described test pieces:

1) Hot workability test

Evaluation of hot workability was effected based on visual observation of whether or not defects such as cracks occur in hot forging. [O] indicates that substantially no defect occurred in hot forging, [×] indicates that large scale cracks were recognized in hot forging and Δ indicates that small cracks occurred in hot forging.

2) Evaluation of machinability

Evaluation of machinability was collectively effected based on cutting resistance in machining, finished surface roughness and chip shapes. A cutting tool made of cermet was used to perform machining under a dry condition at a circumferential speed of 150 m/min, a depth of cutting per revolution of 0.1 mm and a feed rate per revolution of 0.05 mm. A cutting resistance in N as a unit was determined by measuring a cutting force generating in the machining. The finished surface roughness was measured by a method stipulated in JIS B 0601 and a value thereof was an arithmetic average roughness (in μm Ra) on a test piece surface after the machining. Moreover, chip shapes were visually observed and when friability was good, the result is indicated by [G] and when friability is bad and all chips are not separated but partly connected, the result is indicated by [B] and when evaluation of chip shapes is intermidiate of [G] and [B], the result is indicated by [I].

3)

4)Evaluation of out-gas resistivity

Evaluation of out-gas resistivity was performed by determining an amount of released S. To be concrete, test pieces in use each had the shape of a rectangular prism of 15 mm in length, 25 mm in width and 3 mm in thickness and the entire surface of each were polished with No. 400 emery paper. A test piece was placed in a sealed vessel having an inner volume of 250 cm^3 together with a silver foil having a size of 10 mm in length, 5 mm in width and 0.1 mm in thickness and 0.5 cm^3 of pure water, and a temperature in the vessel was maintained at 85°C for 20 hr. A S content W_{S0} in the silver foil after the process for the test was measured by a combustion type infrared absorbing analysis method.

4) Cold workability test

Evaluation of cold workability was performed by measuring a threshold compressive stain in a compression test on specimens Nos. 1 to 5 and 13. Test pieces for compression each had the shape of a cylinder of 15 mm in diameter and 22.5 mm in height and each piece was compressed by a 600 t oil hydraulic press to obtain a threshold compressive strain, wherein the threshold compressive strain is defined as In (H0/H) or a natural logarithm of H0/H, H0 being an initial height of the test piece and H being a threshold height which is a maximum height at which no cracking has occurred. Reference alloys of the specimens Nos. 1 to 5 were confirmed to have high threshold compressive ratios almost equal to comparative steel specimen No. 15 and higher than comparative steel specimen No. 16 by about 20 %, and have a good cold workability as well.

5) Evaluation of corrosion resistivity

Evaluation of corrosion resistivity was performed by a salt spray test. Test pieces each were prepared so to have the shape of a cylinder of 10 mm in diameter and 50 mm in height. The entire surface of each test piece was polished with No. 400 emery paper and cleaned. A test piece was exposed to a fog atmosphere of 5 mass % NaCl aqueous solution at 35°C for 96 hr. Final evaluation was visually performed with the naked eye. As a result, the inventive steel of the present invention was confirmed to maintain good corrosion resistivity. The results are shown in Table 2.

Table 2

[0024] It is found from Table 2 that reference steel is comparable with conventional ferrite containing stainless steel in hot workability, cold workability and corrosion resistivity and moreover, is better in machinability than the conventional ferrite containing stainless steel. Further, it is found from Table 2 when comparing with comparative steel specimens Nos. 16 and 18 that the reference steel is smaller in W_{S0} and better in out-gas resistivity. The reason why kinds of steel of comparative alloy specimens Nos. 16 and 18 each have a high Wso is considered that since the steel of the kinds has neither Ti nor Zr, carbo-sulfide is hard to be formed, whereby a S amount in the matrix is excessively high. In comparative alloy specimen No. 18, hot workability is poor and therefore, evaluation of machinability was not performed.

Example 2 (Fe,Ni) based alloy

[0025] A free cutting alloy of the present invention constituted with Ni based alloy used as (Fe,Ni) based electromagnetic material and (Fe,Ni) based heat resisting material (the fifth selection invention) was prepared in the following way to be applied to tests: First, Test alloy of various compositions in mass % shown in Tables 3, 4 and 5, which is 7 kg blocks, were molten in a high frequency furnace in an Ar stream to be formed into ingots of 80 mm in diameter. Then, the ingots were processed in hot forging at a temperature in the range of 950 to 1100°C into rods having a circle section, 24 mm in diameter. Thereafter, the rods were machined to a diameter of 23 mm, followed by cold rolling into a diameter of 22 mm, to obtain test alloys.

[0026] Further, identification of inclusions in the structure was performed by a method similar to Example 1 (Reference). While main inclusion in inventive steel of the present invention was $(Ti,Zr)_4(S,Se)C_2$, inclusions such as (Ti,Zr)S and $(Ti,Zr)S_3$ were locally recognized. A trace of (Mn,Cr)S was recognized in each of specimens Nos. 2, 14, 19, 29, 36, 39, 49 and 55, all having a high Mn content. An optical microphotograph of a specimen No. 30 of a third selection inventive alloy is shown in Fig. 5.

Table 3

Table 4

Table 5

[0027] Thus obtained Ni based alloys of the compositions were evaluated on not only hot workability and machinability, but also characteristics required of Ni alloy among magnetic characteristics, a thermal expansion coefficient and an elastic constant. Evaluation methods for respective characteristics are as follows:

1) Hot workability test
Evaluation of hot workability was effected based on visual observation of whether or not defects such as cracks occur in hot forging. [O] indicates that substantially no defect occurred in hot forging, [×] indicates that large scale cracks were recognized in hot forging and Δ indicates that so small cracks as to be removed by a grinder occurred in hot forging. A relation between the ranges of the parameters of X and Y defined by the formulae (1) and (2) and evaluation results of hot workability is shown in Fig. 6.
2) Machinability
Machinability was evaluated as follows: a SKH 51 drill of 5 mm in diameter was used on a test piece of steel for machining at a number of revolution of 915 rpm under a load of 415 N on a cutting edge thereof and a time in sec consumed for boring a hole of 10 mm in depth on steel was measured. Machinability was evaluated by a length of the time. A relation between a parameter Y in mass % and a boring time is shown Fig. 7.
3) Magnetic characteristics
Test pieces each in the shape of a ring, of 10 mm in outer diameter, 4.5 mm in inner diameter and 5 mm in thickness were prepared for measurement of magnetic characteristics. A test piece received magnetic annealing at 1000°C and thereafter, direct current magnetic characteristics including a magnetic flux density, a maximum magnetic permeability and a direct current coercive force were measured by a B-H loop tracer: a magnetic flux density B1 (T) under a magnetic field of 1 Oe, a magnetic flux density B5 (T) under a magnetic field of 5 Oe, and a magnetic flux density B10 (T) under a magnetic field of 10 Oe, a maximum magnetic permeability(μm) and a direct current coercive force Hc (A/cm).
4) An evaluation for thermal expansion coefficient and temperature coefficient of Young's modulus
An evaluation for thermal expansion coefficient was performed on the test alloy pieces which were each shaped into a cylinder of 5 mm in diameter and 50 mm in height. The thermal expansion coefficient was measured at temperatures ranging from 0 to 80°C, after the pieces were annealed at 830°C. For measurement of temperature

coefficient of Young's modulus, test alloy pieces were each shaped into a cylinder of 5 mm in diameter and 80 mm in height and thereafter, processed in a solution treatment at 1000°C, followed by rapid cooling. After the rapid cooling, an alloy cylinder as an intermediate was subjected to an aging heat treatment at temperatures from 580 to 590°C into a final test alloy piece. Young's modulus was measured on the test alloy pieces at temperatures ranging from 20 to 100°C using a free resonance elastic modulus tester. The results are shown in Tables 6 and 7.

Table 6

Table 7

[0028] Data of evaluations of hot workability are indicated by plotting of the marks O,Δ and× . A straight line 1 is a boundary line (Y = 0.5 X) of the condition formula (2) and a straight line 2 is a boundary line (0.2 Y = Wc) of the condition formula (3). In the prior art, it was considered that when Ni was included in a large content, hot workability was extremely deteriorated if S was added as a free cutting element. However, when comparing specimens Nos. 1 to 20 of fifth selection inventive alloys of compositions shown in Tables 3, 4 and 5 with specimens Nos. 71 to 75 of reference alloys and specimens Nos. 66 to 70 of comparative alloy, it is found that the fifth selection inventive alloy has hot workability better than the comparative alloys and the reference alloys have, regardless of a magnitude of each of contents of additive elements Si, Mn, Al and Mo, each in the range of 1 % or lower. This is considered because, in such conditions, since a percent of inclusions of carbo-sulfide based $(Ti,Zr)_4C_2(S,Se,Te)_2$ especially stable among sulfide based inclusions is large, formation of (Mn,Cr,Ni)S being a cause for hot-work cracking is controlled. This mechanism was confirmed by actual analysis on components of the inclusions. That is, it is found that machinability is improved in the inventive alloy of the present invention and moreover, not only machinability but also hot workability are improved in the fifth selection inventive alloy.

[0029] Judging from Tables 6 and 7, it is found that while magnetic characteristics of specimens Nos. 9 to 12 of fifth selection inventive alloys with Permalloy B as a base component are almost not deteriorated, machinability is improved by a great margin when compared with the characteristics of Permalloy B alloy shown as a specimen No. 60 of a comparative alloy. While thermal expansion coefficients of specimens Nos. 5 to 8 of fifth selection inventive alloys with low expansion alloy of specimen No. 59 of a comparative alloy similar to Invar alloy as a base composition are also almost not deteriorated, machinability thereof is greatly improved. That is, the fifth selection inventive alloy of the present invention to which Ti and Zr, and S, Se and Te are added so as to satisfy the condition formulae (1) to (3) has no reduction in hot workability and furthermore, almost no deterioration in functional performances inherited from the base alloy.

[0030] It is found that in specimens Nos. 17 to 26 of fifth selection inventive alloys, an effect of improving machinability can be attained even if Cr is added with 12 mass % as the upper limit. For example, specimens Nos. 20 to 23 of fifth selection inventive alloys with specimen No. 61 of a comparative alloy, as a base composition, which is a constant-modulus alloy whose elastic characteristics are constant in the vicinity of room temperature, has not only good hot workability, but also greatly increased machinability, and in addition, a temperature coefficient of a Young's modulus is almost not affected either, thereby enabling use as constant modulus alloy in a proper manner.

[0031] It is found that in specimens Nos. 27 to 36 of fifth selection inventive alloys, even when Co is added with 18 % as the upper limit, good hot workability and the effect of improving machinability can be obtained. Thermal coefficients of specimens Nos. 30 to 33 of fifth selection inventive alloys with a glass sealing agent of a comparative alloy as a base composition receive almost no influence either but the specimens Nos. 30 to 33 improve machinability by a great margin. In such a way, even when Co is added in the range of 18 % or less, none of the effects of the present invention changes and the fifth selection inventive alloy can be preferably used as Invar alloy excellent in machinability. The effect to contain Cr or Co can be exerted when both elements are co-existent as well.

[0032] Fig. 7 is a graph obtained by plotting a drill boring time on alloy in Example 2 against Y in mass %. As can be seen in the graph, when Y is less than 0.01 mass %, it is seen that a boring time tends to accelerate its increase.

Table 1

		C	Si	Mn	P	Cu	Ni	Cr	N	O	Ti	Zr	S	Se	note
reference steel	1	0.029	0.22	0.05	0.01	0.05	0.05	16.7	0.006	0.004	0.58	–	0.21	–	–
	2	0.149	0.18	0.28	0.01	0.19	0.13	19.3	0.016	0.006	1.15	–	0.33	0.13	–
	3	0.103	0.52	0.35	0.02	0.45	0.83	20.5	0.009	0.002	0.52	0.61	0.28	–	0.8Mo
	4	0.021	0.33	0.55	0.02	0.22	0.63	28.3	0.007	0.008	0.14	–	0.05	–	0.16Pb
	5	0.159	0.22	0.29	0.01	1.17	0.04	20.2	0.007	0.009	1.01	0.52	0.42	–	1.8Mo, 0.02Te
	6	0.111	0.87	0.52	0.02	0.13	0.65	18.5	0.004	0.001	1.05	–	0.34	–	2.2W, 0.0018Mg
	7	0.095	0.26	1.79	0.01	0.11	0.33	21.4	0.004	0.005	0.89	–	0.25	0.11	0.11Bi, 0.0027Ca
	8	0.072	0.32	0.43	0.02	0.25	1.21	24.3	0.008	0.005	0.77	–	0.25	–	0.0033B
	9	0.216	0.28	0.18	0.02	0.25	0.25	19.2	0.013	0.009	1.65	–	0.47	0.18	0.11Ta, 0.0025REM
	10	0.100	0.14	0.33	0.02	0.22	0.23	19.0	0.007	0.009	0.85	–	0.28	–	0.23Nb
	11	0.094	0.36	0.85	0.01	0.54	0.13	15.2	0.003	0.011	0.94	–	0.31	–	2.8Mo, 0.25Hf, 0.0022B
	12	0.133	0.29	0.33	0.02	0.42	0.32	22.2	0.002	0.004	1.16	–	0.38	–	1.5Co
	13	0.075	0.49	0.41	0.03	0.31	0.11	17.9	0.012	0.007	0.68	–	0.22	–	0.17Pb, 0.03Te, 2.2Mo
	14	0.096	0.24	0.67	0.02	0.08	0.54	20.2	0.008	0.006	0.82	–	0.28	–	0.26Pb
comparative steel	15	0.002	0.29	0.05	0.02	0.15	0.24	16.5	0.008	0.003	–*	–	–*	–	–
	16	0.002	0.19	0.88	0.02	0.17	0.19	17.2	0.018	0.002	–*	–	0.21	–	–
	17	0.016	0.23	0.29	0.02	0.18	0.25	19.1	0.009	0.005	–*	–	0.32	–	–
	18	0.019	0.33	1.06	0.01	0.25	0.24	18.9	0.011	0.012	–*	–	0.42	–	0.38Pb, 0.15Te

* indicates "outside the scope of the present invention."

Table 2

		hot workability	cutting resistance[N]	finished surface roughness [μm]	chip shape	Wos [mass %]
reference steel	1	○	24.5	1.12	G	0.005
	2	○	21.9	0.95	G	0.014
	3	○	23.8	1.09	G	0.017
	4	○	25.8	1.35	G	0.009
	5	○	19.5	0.81	G	0.011
	6	○	21.8	0.99	G	0.017
	7	○	19.4	0.83	G	0.031
	8	○	25.9	1.32	G	0.019
	9	○	20.0	0.86	G	0.011
	10	○	23.4	1.15	G	0.018
	11	○	23.6	1.09	G	0.023
	12	○	21.6	1.00	G	0.014
	13	○	19.8	0.78	G	0.013
	14	○	20.5	0.90	G	0.015
comparative steel	15	○	35.4	1.87	B	0.002
	16	○	26.3	1.41	G	0.062
	17	○	26.1	1.36	G	0.017
	18	×	—	—	—	0.052

* indicates "outside the scope of the present invention."

Table 3

	C	Si	Mn	P	S	Se	Te	Ni	Cr	Co	Mo	Cu	Al	Ti	Zr	X	Y	C/X	Y/X	remark
1	0.015	0.08	0.23	0.003	0.026	0.000	0.000	20.68	0.05	0.03	0.00	0.02	0.932	0.053	0.000	0.053	0.026	0.276	0.488	fifth selection inventive alloy
2	0.031	0.08	0.92	0.004	0.099	0.008	0.000	20.81	0.03	0.03	0.00	0.02	0.004	0.206	0.011	0.212	0.102	0.147	0.483	
3	0.018	0.10	0.39	0.006	0.085	0.000	0.006	20.34	0.04	0.04	0.00	0.03	0.003	0.221	0.031	0.237	0.086	0.077	0.363	
4	0.026	0.95	0.48	0.003	0.066	0.006	0.007	20.08	0.03	0.03	0.00	0.01	0.003	2.889	0.103	2.943	0.071	0.009	0.024	
5	0.010	0.09	0.51	0.002	0.037	0.000	0.008	35.89	0.04	0.02	0.00	0.02	0.002	0.187	0.000	0.187	0.039	0.051	0.207	
6	0.016	0.14	0.48	0.001	0.034	0.009	0.000	36.13	0.02	0.02	0.00	0.03	0.003	0.187	0.013	0.194	0.038	0.082	0.196	
7	0.292	0.12	0.45	0.003	0.195	0.010	0.008	36.21	0.03	0.03	0.00	0.02	0.003	0.935	0.034	0.953	0.201	0.306	0.211	
8	0.015	0.11	0.52	0.002	0.011	0.000	0.000	36.44	0.03	0.02	0.00	0.02	0.002	0.124	0.112	0.182	0.011	0.083	0.062	
9	0.006	0.13	0.39	0.005	0.021	0.012	0.000	45.64	0.01	0.03	0.00	0.03	0.013	0.155	0.011	0.161	0.026	0.039	0.164	
10	0.015	0.16	0.38	0.004	0.021	0.000	0.013	45.78	0.02	0.03	0.00	0.02	0.016	0.147	0.012	0.153	0.024	0.097	0.158	
11	0.043	0.15	0.43	0.004	0.020	0.010	0.009	46.26	0.01	0.04	0.00	0.01	0.013	0.152	0.011	0.158	0.027	0.274	0.168	
12	0.012	0.11	0.42	0.003	0.007	0.011	0.000	46.31	0.03	0.02	0.00	0.02	0.017	0.156	0.013	0.163	0.012	0.074	0.072	
13	0.015	0.10	0.37	0.005	0.025	0.000	0.013	81.78	0.03	0.03	0.00	0.03	0.912	0.058	0.000	0.058	0.028	0.256	0.491	
14	0.038	0.08	0.93	0.002	0.146	0.008	0.000	81.36	0.04	0.03	0.00	0.02	0.012	0.306	0.011	0.312	0.149	0.122	0.477	
15	0.028	0.96	0.59	0.005	0.123	0.000	0.012	81.41	0.05	0.04	0.00	0.01	0.014	0.278	0.036	0.297	0.126	0.093	0.423	
16	0.026	0.07	0.68	0.004	0.045	0.011	0.000	81.33	0.02	0.02	0.00	0.02	0.011	2.867	0.084	2.911	0.049	0.009	0.017	
17	0.011	0.09	0.47	0.003	0.027	0.000	0.009	20.46	11.32	0.03	0.00	0.02	0.920	0.061	0.000	0.061	0.030	0.176	0.484	
18	0.021	0.92	0.41	0.004	0.086	0.012	0.008	20.17	11.67	0.03	0.00	0.01	0.013	0.290	0.023	0.302	0.093	0.069	0.307	
19	0.032	0.08	0.93	0.003	0.031	0.014	0.005	20.58	11.46	0.02	0.00	0.02	0.016	2.839	0.096	2.889	0.038	0.011	0.013	
20	0.007	0.53	0.46	0.004	0.027	0.000	0.000	42.08	5.21	0.03	0.00	0.03	0.512	2.719	0.007	0.223	0.027	0.032	0.121	
21	0.014	0.56	0.48	0.002	0.025	0.000	0.007	41.63	5.56	0.02	0.00	0.02	0.503	2.715	0.005	0.218	0.027	0.066	0.124	
22	0.298	0.51	0.44	0.003	0.152	0.011	0.006	42.13	5.14	0.04	0.00	0.01	0.523	3.885	0.005	1.388	0.158	0.215	0.114	
23	0.029	0.59	0.47	0.003	0.010	0.005	0.003	41.88	5.33	0.03	0.00	0.02	0.516	2.726	0.006	0.229	0.013	0.128	0.058	
24	0.010	0.21	0.39	0.005	0.022	0.005	0.005	76.51	11.21	0.03	0.00	0.01	0.965	0.052	0.000	0.052	0.025	0.193	0.477	
25	0.021	0.93	0.41	0.004	0.088	0.009	0.008	73.63	11.74	0.02	0.00	0.03	0.017	0.344	0.015	0.352	0.094	0.061	0.267	
26	0.038	0.28	0.96	0.005	0.015	0.010	0.008	81.08	4.36	0.03	0.00	0.02	0.015	2.872	0.138	2.944	0.021	0.013	0.007	

Table 4

	C	Si	Mn	P	S	Se	Te	Ni	Cr	Co	Mo	Cu	Al	Ti	Zr	X	Y	C/X	Y/X	remark
27	0.011	0.07	0.31	0.004	0.025	0.000	0.008	20.41	0.04	17.55	0.00	0.02	0.941	0.055	0.000	0.055	0.027	0.208	0.482	
28	0.025	0.94	0.38	0.005	0.106	0.008	0.007	20.58	0.03	17.34	0.00	0.04	0.013	0.284	0.014	0.291	0.111	0.086	0.381	
29	0.041	0.08	0.92	0.004	0.074	0.011	0.000	20.38	0.06	17.73	0.00	0.03	0.005	2.848	0.110	2.905	0.078	0.014	0.027	
30	0.012	0.12	0.23	0.005	0.032	0.000	0.000	32.42	0.02	5.41	0.00	0.03	0.004	0.214	0.000	0.214	0.032	0.058	0.151	
31	0.031	0.14	0.19	0.004	0.052	0.005	0.005	32.04	0.02	5.24	0.00	0.02	0.003	0.233	0.009	0.238	0.055	0.132	0.233	
32	0.294	0.10	0.21	0.003	0.302	0.009	0.011	32.13	0.01	5.57	0.00	0.02	0.003	1.230	0.013	1.237	0.308	0.238	0.249	
33	0.037	0.13	0.20	0.005	0.005	0.009	0.010	32.26	0.03	5.63	0.00	0.03	0.004	0.272	0.012	0.278	0.011	0.133	0.039	
34	0.010	0.15	0.31	0.006	0.022	0.000	0.008	70.43	0.03	17.58	0.00	0.02	0.937	0.054	0.000	0.054	0.024	0.188	0.453	
35	0.029	0.94	0.42	0.004	0.109	0.008	0.012	81.71	0.02	5.73	0.00	0.04	0.005	0.332	0.022	0.343	0.116	0.085	0.337	
36	0.046	0.18	0.91	0.005	0.051	0.009	0.000	81.76	0.03	2.76	0.00	0.02	0.004	2.392	0.936	2.879	0.055	0.016	0.019	
37	0.008	0.09	0.38	0.005	0.019	0.007	0.008	20.63	0.03	0.04	2.84	6.63	0.911	0.051	0.000	0.051	0.024	0.164	0.468	
38	0.033	0.96	0.31	0.004	0.129	0.007	0.008	20.51	0.03	0.04	6.87	1.55	0.006	0.410	0.027	0.424	0.134	0.079	0.316	
39	0.035	0.07	0.92	0.006	0.042	0.006	0.007	20.22	0.02	0.03	0.00	0.03	0.014	2.807	0.206	2.914	0.047	0.012	0.016	fifth selection inventive alloy
40	0.012	0.08	0.52	0.004	0.042	0.012	0.000	78.28	0.03	0.04	4.58	3.48	0.967	0.160	0.012	0.166	0.047	0.071	0.284	
41	0.026	0.06	0.50	0.003	0.043	0.006	0.000	78.14	0.04	0.03	4.58	3.59	0.003	0.156	0.010	0.161	0.045	0.162	0.281	
42	0.296	0.07	0.51	0.003	0.307	0.007	0.009	77.94	0.04	0.04	4.46	3.51	0.004	1.121	0.011	1.127	0.312	0.263	0.277	
43	0.028	0.05	0.50	0.003	0.010	0.000	0.000	78.36	0.05	0.04	4.51	3.46	0.005	0.169	0.011	0.175	0.010	0.159	0.059	
44	0.013	0.16	0.28	0.005	0.026	0.000	0.009	81.13	0.05	0.04	2.01	4.42	0.941	0.059	0.000	0.059	0.029	0.223	0.486	
45	0.010	0.91	0.31	0.006	0.036	0.007	0.008	81.59	0.03	0.03	3.58	2.33	0.017	0.176	0.012	0.182	0.041	0.053	0.224	
46	0.046	0.06	0.93	0.005	0.087	0.008	0.000	81.35	0.05	0.04	0.00	0.02	0.012	2.804	0.189	2.902	0.090	0.016	0.031	
47	0.009	0.07	0.33	0.005	0.023	0.010	0.000	20.24	0.03	17.71	0.00	0.02	0.928	0.056	0.000	0.056	0.027	0.153	0.483	
48	0.015	0.97	0.31	0.004	0.067	0.000	0.011	20.38	11.83	0.05	0.00	0.03	0.011	0.195	0.018	0.204	0.070	0.075	0.341	
49	0.024	0.07	0.96	0.003	0.050	0.010	0.009	20.54	0.04	0.02	6.51	0.03	0.014	0.320	0.021	0.331	0.056	0.072	0.169	
50	0.292	0.08	0.29	0.004	0.277	0.007	0.006	20.49	0.03	0.03	0.00	6.92	0.008	1.578	0.020	1.588	0.281	0.184	0.177	
51	0.037	0.07	0.30	0.006	0.011	0.000	0.000	20.55	0.05	0.02	0.00	0.05	0.011	0.338	0.019	0.348	0.011	0.105	0.033	
52	0.047	0.20	0.23	0.004	0.062	0.000	0.000	20.16	0.02	0.03	0.00	0.04	0.018	2.885	0.157	2.967	0.062	0.016	0.021	

Table 5

	C	Si	Mn	P	S	Se	Te	Ni	Cr	Co	Mo	Cu	Al	Ti	Zr	X	Y	C/X	Y/X	remark
53	0.008	0.21	0.23	0.004	0.028	0.000	0.000	81.01	0.03	7.43	0.00	0.04	0.905	0.058	0.000	0.058	0.028	0.136	0.479	fifth selection inventive alloy
54	0.011	0.91	0.37	0.005	0.035	0.008	0.000	81.43	0.04	6.89	0.00	0.04	0.013	0.205	0.011	0.211	0.038	0.053	0.182	
55	0.040	0.15	0.97	0.004	0.049	0.000	0.009	81.27	0.03	0.03	6.72	0.03	0.010	0.317	0.011	0.323	0.051	0.123	0.158	
56	0.293	0.31	0.42	0.006	0.160	0.007	0.008	81.62	1.44	1.39	1.24	2.91	0.021	1.249	0.013	1.256	0.165	0.233	0.131	
57	0.053	0.06	0.44	0.005	0.014	0.000	0.000	81.35	0.05	0.03	0.00	0.03	0.012	0.296	0.012	0.302	0.014	0.174	0.048	
58	0.052	0.07	0.31	0.004	0.063	0.000	0.000	81.53	0.02	0.05	0.00	0.03	0.011	2.848	0.056	2.877	0.063	0.018	0.022	
59	0.005	0.16	0.48	0.005	0.009	0.000	0.000	36.27	0.03	0.02	0.00	0.02	0.009	0.198	0.011	0.204	0.009	0.103	0.044	comparative alloy
60	0.006	0.06	0.39	0.006	0.003	0.000	0.000	46.58	0.03	0.03	0.00	0.03	0.012	0.005	0.000	0.005	0.003	1.602	0.603	
61	0.005	0.52	0.41	0.006	0.005	0.000	0.000	42.18	5.12	0.03	0.00	0.03	0.511	2.325	0.301	2.482	0.005	0.004	0.002	
62	0.007	0.21	0.24	0.007	0.013	0.000	0.000	32.31	0.03	5.04	0.00	0.02	0.009	0.030	0.000	0.030	0.013	0.167	0.445	
63	0.008	0.05	0.52	0.006	0.006	0.000	0.000	78.13	0.02	0.03	4.51	3.42	0.008	0.181	0.013	0.188	0.006	0.956	0.033	
64	0.006	0.03	0.41	0.007	0.008	0.000	0.000	21.03	0.02	0.02	0.00	0.01	0.080	0.211	0.000	0.211	0.008	0.882	0.038	
65	0.007	0.04	0.42	0.005	0.008	0.000	0.000	81.32	0.03	0.04	0.00	0.02	0.009	0.188	0.014	0.195	0.008	0.901	0.041	
66	0.023	0.08	0.49	0.003	2.284	0.008	0.000	35.89	0.03	0.02	0.00	0.02	0.003	0.836	0.000	0.836	2.287	0.028	2.736	
67	0.022	0.14	0.41	0.006	2.262	0.012	0.000	45.84	0.02	0.02	0.00	0.04	0.011	0.944	0.010	0.949	2.267	0.023	2.389	
68	0.059	0.51	0.48	0.005	0.433	0.000	0.000	42.07	5.17	0.03	0.00	0.02	0.508	3.673	0.000	3.673	0.433	0.016	0.118	
69	0.130	0.11	0.25	0.004	2.272	0.000	0.000	32.35	0.02	5.36	0.00	0.02	0.007	3.712	0.000	3.712	2.272	0.035	0.612	
70	0.007	0.07	0.51	0.003	0.044	0.000	0.000	78.05	0.04	0.03	4.51	3.52	0.007	0.158	0.000	0.158	0.044	0.047	0.277	reference alloy
71	0.021	0.91	0.55	0.004	0.123	0.000	0.000	81.23	0.03	0.03	0.00	0.02	0.012	0.281	0.000	0.281	0.123	0.073	0.438	
72	0.012	0.06	0.35	0.003	0.030	0.000	0.000	20.15	0.03	17.21	0.00	0.02	0.884	0.058	0.000	0.058	0.030	0.211	0.523	
73	0.011	0.07	0.49	0.004	0.034	0.000	0.000	20.29	11.58	0.03	0.00	0.02	0.957	0.064	0.000	0.064	0.034	0.176	0.531	
74	0.016	0.09	0.25	0.003	0.030	0.000	0.000	20.77	0.04	0.02	0.00	0.03	0.912	0.057	0.000	0.057	0.030	0.288	0.524	
75	0.009	0.08	0.91	0.004	0.109	0.000	0.000	81.15	0.04	0.03	0.00	0.03	0.014	2.953	0.000	2.953	0.109	0.003	0.037	

Table 6

	(hot warkability)	(machinability) boring time (sec)	thermal expansion coefficient ($\times 10^{-7}$/K)	temperature coefficient of Young's modulus (10^{-5}/K)	magnetic characteristics					remark
					B1 (T)	B5 (T)	B10 (T)	μm (T)	Hc (A/cm)	

1	○	16.7	—	—	—	—	—	—	—	
2	○	11.3	—	—	—	—	—	—	—	
3	○	10.9	—	—	—	—	—	—	—	
4	○	10.7	—	—	—	—	—	—	—	
5	○	20.4	7.57	—	—	—	—	—	—	
6	○	21.5	7.21	—	—	—	—	—	—	
7	○	14.3	7.86	—	—	—	—	—	—	
8	○	27.7	8.22	—	—	—	—	—	—	
9	○	28.5	—	—	1.05	1.30	1.39	26,100	0.14	
10	○	23.9	—	—	0.99	1.25	1.36	25.900	0.16	
11	○	28.3	—	—	0.92	1.19	1.31	23,500	0.17	
12	○	29.3	—	—	0.95	1.21	1.33	24.500	0.15	
13	○	17.4	—	—	—	—	—	—	—	
14	○	12.0	—	—	—	—	—	—	—	
15	○	12.3	—	—	—	—	—	—	—	
16	○	14.8	—	—	—	—	—	—	—	
17	○	15.4	—	—	—	—	—	—	—	
18	○	11.2	—	—	—	—	—	—	—	
19	○	14.8	—	—	—	—	—	—	—	
20	○	26.5	—	±1	—	—	—	—	—	fifth selection inventive alloy
21	○	26.4	—	±1	—	—	—	—	—	
22	○	17.5	—	±1	—	—	—	—	—	
23	○	26.8	—	±1	—	—	—	—	—	
24	○	13.8	—	—	—	—	—	—	—	
25	○	11.3	—	—	—	—	—	—	—	
26	○	18.6	—	—	—	—	—	—	—	
27	○	12.1	—	—	—	—	—	—	—	
28	○	9.1	—	—	—	—	—	—	—	

Table 7

	(hot workability)	(machinability) boring time (sec)	thermal coefficient ($\times 10^{-7}$/K)	temperature coefficient of Young' s modulus (10^{-5}/K)	magnetic characteristics					remark
					B1 (T)	B5 (T)	B10 (T)	μm (T)	Hc (A/cm)	
41	○	24.4	—	—	—	—	—	121,000	0.013	fifth selection inventive alloy
42	○	13.2	—	—	—	—	—	112,000	0.017	
43	○	27.9	—	—	—	—	—	120,000	0.014	
44	○	26.8	—	—	—	—	—	—	—	
45	○	12.6	—	—	—	—	—	—	—	
46	○	13.3	—	—	—	—	—	—	—	
47	○	13.2	—	—	—	—	—	—	—	
48	○	10.2	—	—	—	—	—	—	—	
49	○	12.5	—	—	—	—	—	—	—	
50	○	10.8	—	—	—	—	—	—	—	
51	○	15.9	—	—	—	—	—	—	—	
52	○	11.3	—	—	—	—	—	—	—	
53	○	22.3	—	—	—	—	—	—	—	
54	○	23.1	—	—	—	—	—	—	—	
55	○	18.3	—	—	—	—	—	—	—	
56	○	17.6	—	—	—	—	—	—	—	
57	○	20.6	—	—	—	—	—	—	—	
58	○	15.1	—	—	—	—	—	—	—	

Table continued

	(hot workability)	(machinability) boring time (sec)	thermal coefficient (×10⁻⁷/K)	temperature coefficient of Young' s modulus (10⁻⁵/K)	magnetic characteristics					remark
					B1 (T)	B5 (T)	B10 (T)	µm (T)	Hc (A/cm)	
59	○	27.4	7.76	—	—	—	—	—	—	comparative alloy
60	○	25.8	—	—	1.13	1.35	1.42	28.300	0.12	
61	○	27.6	—	±1	—	—	—	—	—	
62	○	19.1	4.21	—	—	—	—	—	—	
63	○	33.8	—	—	—	—	—	12,600	0.013	
64	○	20.8	—	—	—	—	—	—	—	
65	○	25.4	—	—	—	—	—	—	—	
66	×	—	—	—	—	—	—	—	—	
61	×	—	—	—	—	—	—	—	—	
68	×	—	—	—	—	—	—	—	—	
69	×	—	—	—	—	—	—	—	—	
70	×	—	—	—	—	—	—	—	—	
71	Δ	11.8	—	—	—	—	—	—	—	reference alloy
72	Δ	12.7	—	—	—	—	—	—	—	
73	Δ	15.3	—	—	—	—	—	—	—	
74	Δ	16.8	—	—	—	—	—	—	—	
75	Δ	12.9	—	—	—	—	—	—	—	

Claims

1. Free cutting alloy containing: 20 to 82 mass % Ni; one or more of Ti and Zr in the range satisfying the relation $0.05 \leq X \leq 3$; one or more of S, Se and Te in the range satisfying the relation $0.01 \leq Y \leq 0.5$ X;
C in the range satisfying the relation $0.2\ Y \leq W \leq 0.3$, wherein a Ti content is indicated by W_{Ti} in mass %, a Zr content by W_{Zr} in mass %, a C content by W_C in mass %, a S content by W_S in a mass %, a Se content by W_{Se} in a mass % and a Te content by W_{Te} in a mass %, the following formulas are given in order to define X and Y:

$$X\ (\text{mass}\ \%) = W_{Ti} + 0.52\ W_{Zr}$$

and

$$Y\ (\text{mass}\ \%) = W_S + 0.41\ W_{Se} + 0.25\ W_{Te};$$

and further containing one or more of Si, Mn and Al in the respective ranges of 1 mass % or lower for Si; 1 mass % or lower for Mn; and 1 mass % or lower for Al; optionally further containing: one or more of Mo and Cu in the respective ranges of 7 mass % or lower for Mo and 7 mass % or lower for Cu; 12 mass % or lower Cr; 18 mass % or lower Co, the balance being Fe and unavoidable impurities;
and wherein a (Ti, Zr) based compound containing one or more of Ti and Zr as a metal element component, C being an indispensable element as bonding component with the metal element component, and one or more of S, Se and Te, said compound is dispersed in the matrix metal phase.

2. Free cutting alloy according to claim 1, wherein the C content is set in the range of Y/4 to 0.2 mass %.

3. Free cutting alloy according to any of claims 1 to 2, wherein the C content is set in the range of Y/4 to Y/2 mass %.

4. Free cutting alloy according to any of claims 1 to 3, wherein a particle size of the (Ti,Zr) based compound as observed in the structure of a polished section of the alloy is in the range of 0.1 to 30 μm on the average, and further an area ratio of the compound in the structure is in the range of 1 to 20%.

Patentansprüche

1. Automatenlegierung, enthaltend: 20 bis 82 Massen-% Ni; ein oder mehrere aus Ti und Zr in dem Bereich, welcher die Beziehung $0{,}05 \leq X \leq 3$ erfüllt;
ein oder mehrere aus S, Se und Te in dem Bereich, welcher die Beziehung $0{,}01 \leq Y \leq 0{,}5$ X erfüllt;
C in dem Bereich, welcher die Beziehung $0{,}2\ Y \leq W_C \leq 0{,}3$ erfüllt, worin ein Ti-Gehalt durch W_{Ti} in Massen-% angegeben ist, ein Zr-Gehalt durch W_{Zr} in Massen-% angegeben ist, ein C-Gehalt durch W_C in Massen-% angegeben ist, ein S-Gehalt durch W_S in Massen-% angegeben ist, ein Se-Gehalt durch W_{Se} in Massen-% angegeben ist und ein Te-Gehalt durch W_{Te} in Massen-% angegeben ist, wobei die folgenden Formeln angegeben sind, um X und Y zu definieren:

$$X\ (\text{Massen-\%}) = W_{Ti} + 0{,}52\ W_{Zr}$$

und

$$Y\ (\text{Massen-\%}) = W_S + 0{,}41\ W_{Se} + 0{,}25\ W_{Te};$$

und weiterhin enthaltend:

ein oder mehrere aus Si, Mn und Al in den jeweiligen Bereichen von 1 Massen-% oder weniger für Si; 1 Massen-% oder weniger für Mn; und 1 Massen-% oder weniger für Al; wahlweise weiterhin enthaltend:

ein oder mehrere aus Mo und Cu in den jeweiligen Bereichen von 7 Massen-% oder weniger für Mo und 7 Massen-% oder weniger für Cu;
12 Massen-% oder weniger Cr;
18 Massen-% oder weniger Co, wobei der Rest Fe und unvermeidbare Verunreinigungen sind;
und worin eine (Ti, Zr)-basierte Verbindung, enthaltend ein oder mehrere aus Ti und Zr als eine Metall-Element-Komponente, wobei C ein unvermeidbares Element als Bindungs-Komponente mit der Metall-Element-Komponente darstellt, und ein oder mehrere aus S, Se und Te, wobei die Verbindung in der Matrix-Metallphase dispergiert ist.

2. Automatenlegierung nach Anspruch 1, worin der C-Gehalt in dem Bereich von Y/4 bis 0,2 Massen-% eingestellt ist.

3. Automatenlegierung nach einem der Ansprüche 1 bis 2, worin der C-Gehalt in dem Bereich von Y/4 bis Y/2 Massen-% eingestellt ist.

4. Automatenlegierung nach einem der Ansprüche 1 bis 3, worin eine Teilchengröße der (Ti, Zr)-basierten Verbindung, wie sie in der Struktur eines polierten Abschnitts der Legierung beobachtet wird, in dem durchschnittlichen Bereich von 0,1 bis 30 μm liegt und worin weiterhin ein Flächenverhältnis der Verbindung in der Struktur in dem Bereich von 1 bis 20% liegt.

Revendications

1. Alliage de décolletage contenant : de 20 à 82 % en masse de Ni ;
un ou plusieurs éléments choisis parmi Ti et Zr dans la plage satisfaisant à la relation $0,05 \leq X \leq 3$;
un ou plusieurs éléments choisis parmi S, Se et Te dans la plage satisfaisant à la relation $0,01 \leq Y \leq 0,5X$;
C dans la plage satisfaisant à la relation $0,2\,Y \leq W_C \leq 0,3$, la teneur en Ti étant représentée par W_{Ti} en % en masse, la teneur en Zr par W_{Zr} en % en masse, la teneur en C par W_C en % en masse, la teneur en S par W_S en % en masse, la teneur en Se par W_{Se} en % en masse et la teneur en Te par W_{Te} en % en masse, les formules suivantes étant mentionnées pour définir X et Y :

$$X\ (\%\ \text{en masse}) = W_{Ti} + 0{,}52W_{Zr},$$

et

$$Y\ (\%\ \text{en masse}) = W_S + 0{,}41W_{Se} + 0{,}25W_{Te}\ ;$$

et contenant en outre :

un ou plusieurs éléments choisis parmi Si, Mn et Al dans les plages respectives de 1 % en masse ou moins pour Si ; 1 % en masse ou moins pour Mn ; et 1 % en masse ou moins pour Al; et contenant en outre éventuellement :

un ou plusieurs éléments choisis parmi Mo et Cu dans les plages respectives de 7 % en masse ou moins pour Mo et de 7 % en masse ou moins pour Cu ;
12 % en masse ou moins de Cr ;
18 % en masse ou moins de Co, le reste consistant en Fe et en impuretés inévitables ; et dans lequel :

un composé de (Ti, Zr) contenant au moins un élément choisi parmi Ti et Zr en tant que composant de type élément de métal, est dispersé dans la phase métallique formant matrice, C étant un élément indispensable comme composant de liaison avec le composant de type élément de métal, et un ou plusieurs éléments choisis parmi S, Se et Te.

2. Alliage de décolletage selon la revendication 1, dans lequel la teneur en C est ajustée dans la plage de Y/4 à 0,2 % en masse.

3. Alliage de décolletage selon l'une quelconque des revendications 1 à 2, dans lequel la teneur en C est ajustée dans la plage de Y/4 à Y/2 % en masse.

4. Alliage de décolletage selon l'une quelconque des revendications 1 à 3, dans lequel la taille particulaire du composé de (Ti, Zr) observé dans la structure d'une section polie de l'alliage, est dans la plage de 0,1 à 30 μm en moyenne, et la proportion de surface du composé dans la structure est en outre dans la plage de 1 à 20 %.

Fig. 1

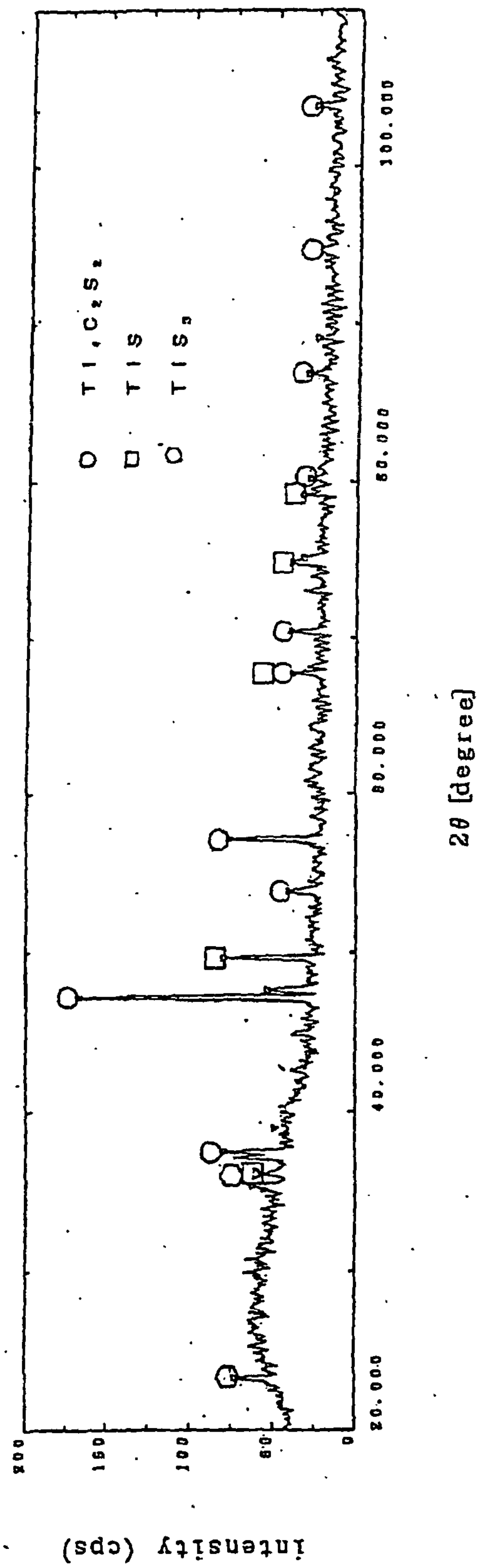
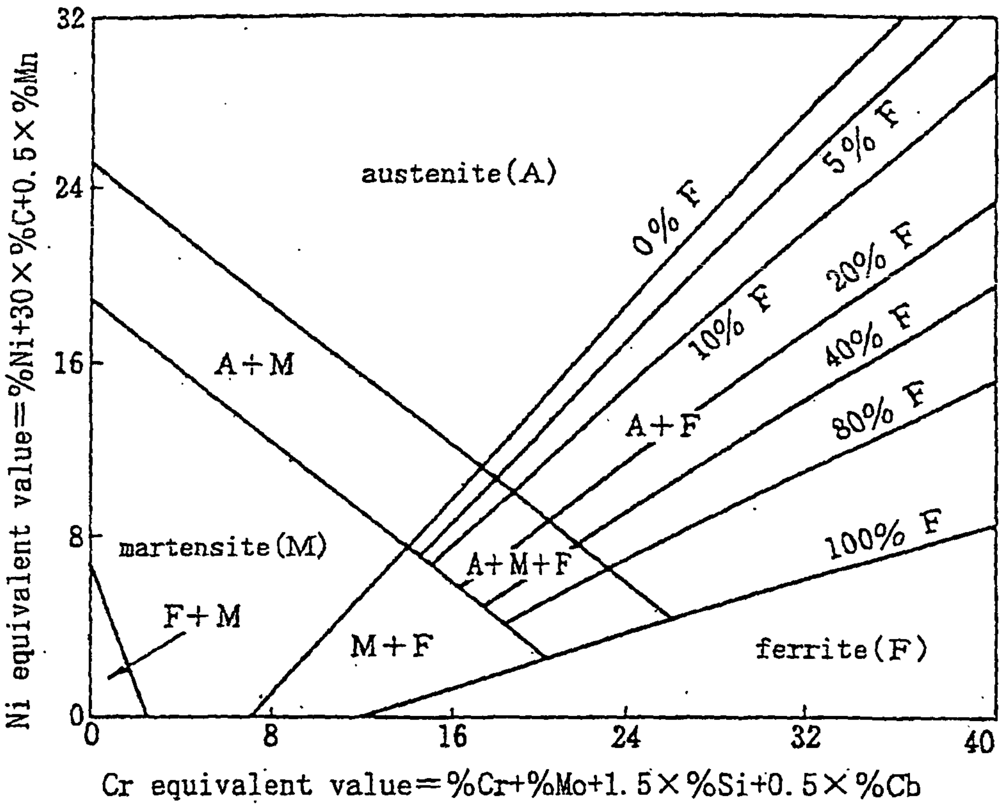

Ti4C2S2
TiS
TiS3
20.000
40.000
60.000
80.000
100.000
2θ [degree]
0
50
100
150
200
intensity (cps)

Fig. 2



structure of stainless steel deposited metals

Fig. 3

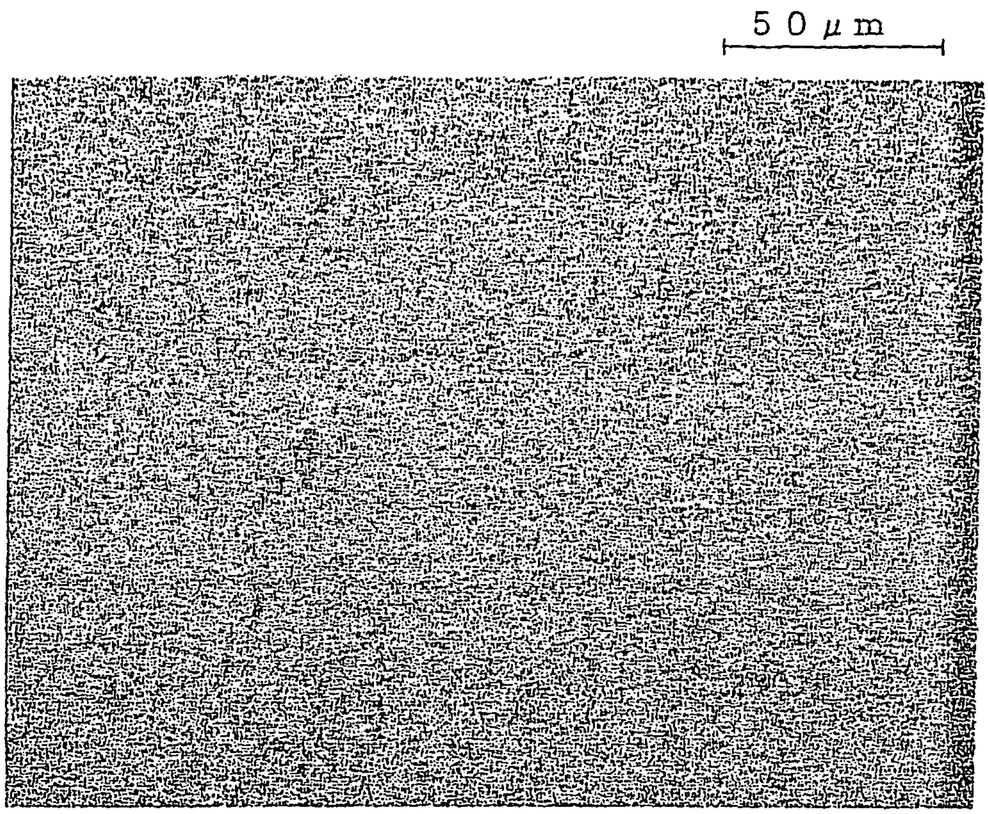
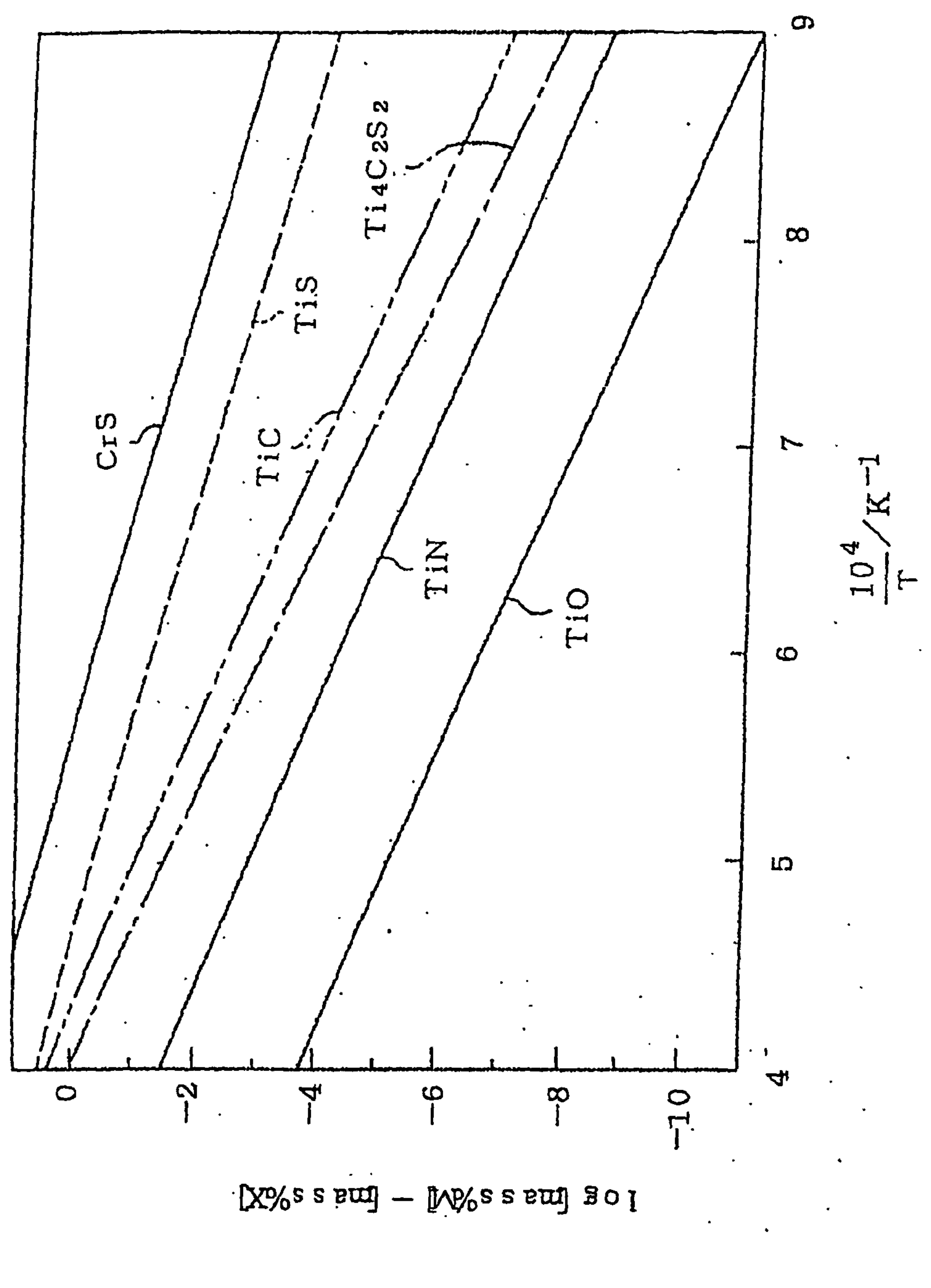


Fig. 4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TiS
TiC
Ti4C2S2
TiN
TiO
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−2
−4
−6
−8
−10
4
5
6
7
8
9
log [mass%M] − [mass%X]
10^4/T /K^−1

Fig. 5

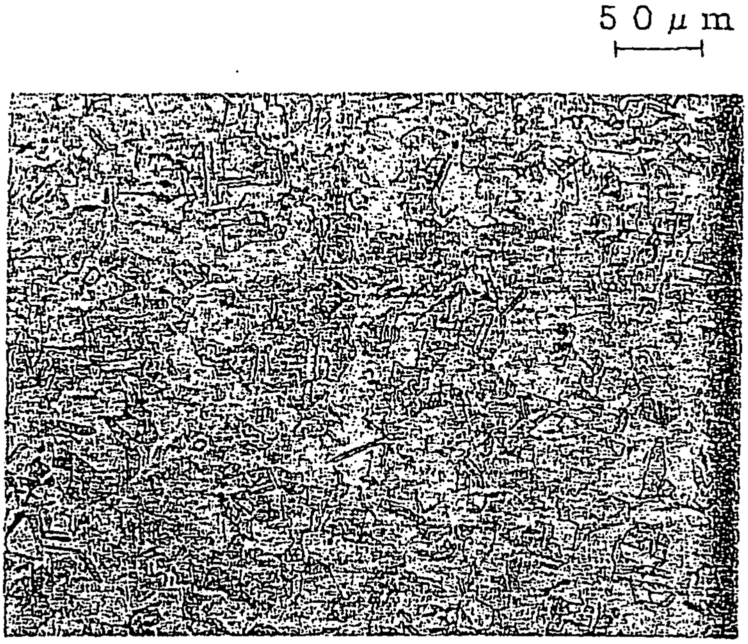


Fig. 6

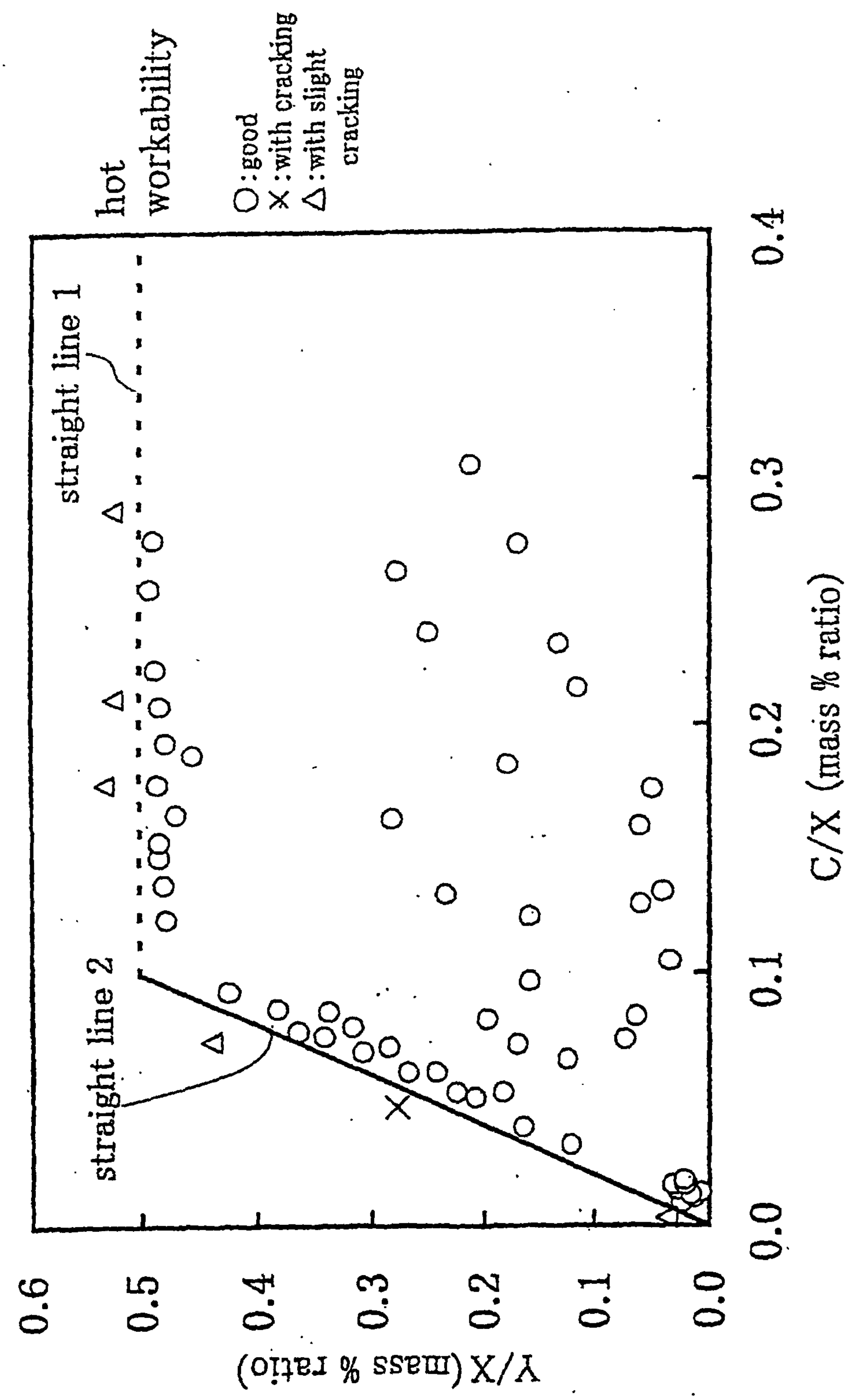
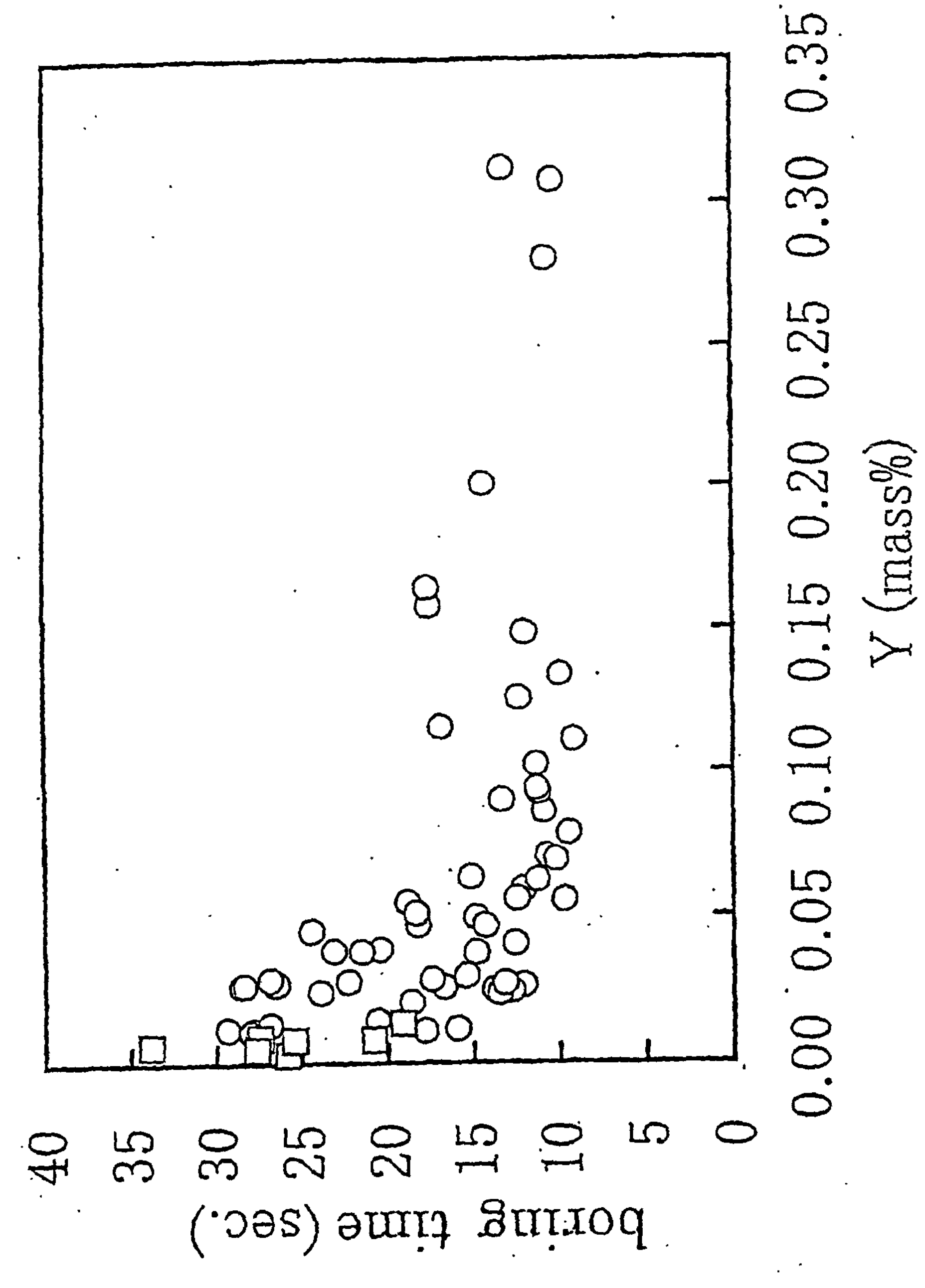

hot workability
○ : good
× : with cracking
Δ : with slight cracking
straight line 1
straight line 2
Y/X (mass % ratio)
C/X (mass % ratio)
0.0
0.1
0.2
0.3
0.4
0.5
0.6

Fig. 7


boring time (sec.)
40
35
30
25
20
15
10
5
0
Y (mass%)
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35